

Easy synthesis of dendrimer-like polymers through a divergent iterative “end-grafting” method†

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We report here an easy method for the synthesis of dendrimer-like polymers with high branching functionality (1 → 8). The synthetic process involves iterative grafting reactions in a divergent way. A multi-functional core containing short segments of polyisoprene (PI), either as a star-like block copolymer of isoprene and styrene or as a linear triblock copolymer of isoprene, styrene and isoprene (coded **G1**), is epoxidized on the double bonds and grafted with a living block copolymer, polyisoprene-*b*-polystyrenyllithium (PI-*b*-PSLi), again with a short PI segment, through the ring-opening reaction of oxirane by polymeric anions. The resulting graft polymer, **G2**, possesses a definite number of PI segments at the periphery. These PI segments are further epoxidized followed by the ring-opening addition of PI-*b*-PSLi, affording **G3**. Repeating the process leads to the synthesis of a dendrimer-like polystyrene up to 5th generation with a polydispersity lower than 1.21, as measured by SEC. A feature of the process is the easily accessible high chain density in the final product, although defects exist due to steric hindrance in the reactions of high generations. The solution properties of the dendritic products are investigated using viscometry and dynamic and static laser light scattering on the molecular conformation. The results support a compact globular conformation model for the dendrimer-like products. In addition, the chain density of the products from the star-like core is higher than that of products from a linear triblock core. AFM results show that the dendritic products adopt flattened conformations and tend to form lateral sphere-like aggregates on mica substrate.

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Introduction

Dendrimer-like star polymers are polymeric analogues of dendrimers in which successive generations are connected by long chain spacers.¹ These polymers have larger molecular weights and sizes relative to those of regular dendrimers. In addition, the dendrimer effect, such as the multiplicity of periphery groups and low intrinsic viscosity relative to their linear counterparts, is retained.

Compared with regular dendrimers, the synthesis of dendrimer-like polymers is complicated by the incorporation of polymer chains into the dendritic structure. The incorporation of polymer chains is associated with the divergent or convergent branching reaction through either *in situ* polymerization or a separate polymerization process (“arm-first”). Divergent branching combined with *in situ* polymerization has been employed in the synthesis of a series of poly(ethylene oxide)

(PEO)-,² polystyrene-³ polycaprolactone (PCL)-,⁴ and polylactide-based^{4,5} dendrimer-like (co)polymers, using multifunctional stars as the core and anionic ring opening polymerization (ROP) or atom transfer radical polymerization (ATRP) to form the chains. More specifically, Percec developed a TERMINI (TERminator Multifunctional INItiator) method in which chain branching was achieved *via* terminating living radical polymerization by a masked difunctional initiator followed by further polymerization, affording dendrimer-like PMMAs.⁶ The divergent branching combined with the iterative “grafting-onto” method has been developed by Hirao and co-workers using “arm-first” anionic polymerization.^{1b,7} This method can produce dendrimer-like (co)polymers with expected molecular weights, mostly polymethacrylates. Furthermore, polymers bearing azide and alkyne termini have been used as building blocks in the preparation of polymeric dendrons, dendrimers and dendrimer-like miktoarm star terpolymers in a divergent way by using Huisgen “click” chemistry.^{1d,8,9}

In contrast, the convergent method usually involves the coupling of terminal functionalized or living polymeric precursors. Hadjichristidis succeeded in preparing dendrimer-like star polymers by coupling anionic living polymers or living stars using chlorosilane derivatives.¹⁰ Knauss achieved continuous coupling of polystyryl anions in the preparation of

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dendritic polystyrene by multi-batch addition of a styrenic functional branching agent into the anionic polymerization of styrene.¹¹ Hutchings and co-workers developed an “arm-first” convergent method in their synthesis of DendriMac PS, in which two kinds of arms with reactive chloride- and biphenol-functionalities were prepared by anionic polymerization.¹² Dendrimer-like copolymers and terpolymers were also synthesized by convergent click chemistry between alkynyl or azide functionalized star polymers onto a core with double or multi-functional azide or alkynyl groups.¹³

In a previous study, we developed a continuous anionic living process for the fast synthesis of dendrimer-like star polymers.¹⁴ By using an anionic inimer as the branching agent, the synthesis of dendritic polystyrene is greatly accelerated (*e.g.*, G5.0 with 32 terminal groups was obtained within 12 hours). In addition, the terminal anions can be used as initiators for the polymerization of diene or methacrylate to prepare dendrimer-like star block copolymers such as PS-*b*-PI, PS-*b*-PMMA, and dendrimer-like star polymers with graft-on-graft peripheries. However, the continuous method suffers from pseudo-gel formation at relatively high generations with multiple peripheral anions, which inhibits further polymerization due to the heterogeneity of the reaction mixture once the pseudo-gel forms.

In this study, we explore a novel approach to synthesize dendrimer-like polymers through a divergent “grafting-onto” strategy. The grafting, or branching reaction, is fulfilled through the ring-opening reaction of multiple oxirane groups at the ends of the preceding generations by the addition of polyisoprene-*b*-polystyryllithium (PI-*b*-PSLi). Hence, no specially synthesized branching agent is needed. One of the merits of this synthetic procedure is that it does not involve a multi-anion intermediate species and is thus free of pseudo-gels. Although the number of branches may vary among different branch points, the “end-grafting” approach is simple and useful in preparing dendrimer-like polymers with high molecular weights and regular shapes, as illustrated by light scattering results.

Results and discussion

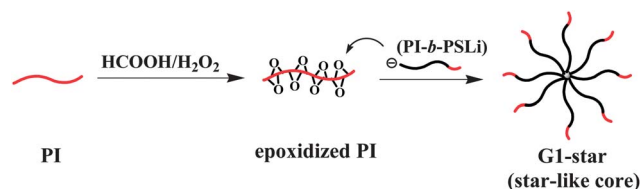
Dendrimer-like polymers are synthesized from two kinds of cores, a star-like core containing eight or nine arms (number average) of block copolymer of styrene and isoprene and a linear core derived

from an ABA type block copolymer of styrene and isoprene. As shown in Scheme 1, the overall procedure includes mainly two iterative steps: (a) the epoxidation of the double bonds in the PI segments using HCOOH/H₂O₂ and (b) the grafting reaction through the nucleophilic ring opening reaction of multiple oxirane groups by a living block copolymer, PI-*b*-PSLi, as branches. The process involves only commonly used monomers and oxidant, and is free of purposely synthesized branching agent.

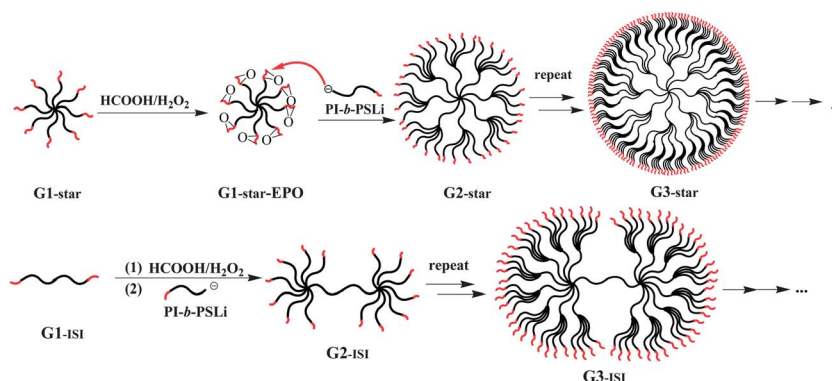
The star-like core is synthesized by grafting a living block copolymer, PI₈-*b*-PS₄₉Li, where the subscripts denote the number average degree of polymerization (DP), onto a short PI homopolymer (number average DP_n = 8 and PDI = 1.07, prepared by *s*-BuLi initiated anionic polymerization of isoprene) through successive epoxidation and ring-opening grafting reactions, as shown in Scheme 2. The molecular weight of the star-like core measured by static light scattering is 5.0 × 10⁴ g mol⁻¹, which corresponds to nine arms per molecule.

The linear triblock core PI₈-*b*-PS₂₇₁-*b*-PI₈, and the living arms, PI-*b*-PSLi, are synthesized by sequential anionic polymerization of styrene and isoprene. The total molecular weight of the triblock core is 29.4 × 10³ g mol⁻¹. The number average molecular weights of PI-*b*-PSLi are M_{n,NMR} = 5.7 × 10³ and 8.5 × 10³ g mol⁻¹ (corresponding to PI₈-*b*-PS₄₉Li and PI₈-*b*-PS₇₆Li, respectively) with PDI = 1.09 and 1.10 determined by SEC, respectively. In order to keep the structural homogeneity, all PI segments used throughout the synthesis come from the same stock solution of PI₈Li or they are prepared under identical conditions. The branches within each dendrimer-like product are derived from the same PI-*b*-PSLi, although they may differ between products.

Both the triblock and star-like cores are epoxidized using HCOOH/H₂O₂. The reagents oxidize double bonds in the 1,4-structure of the PI segment into epoxy groups that undergo



Scheme 2 Synthesis of the star-like core.



Scheme 1 Synthesis of dendrimer-like PS from star-like core (upper) and ISI triblock core (lower).

subsequent ring-opening grafting reactions with PI-*b*-PSLi.¹⁵ The procedure is monitored by ¹H NMR and SEC. Fig. 1 shows the NMR spectra, focused on the vinylic and epoxy protons in the products of different generations, using an ABA-type linear core. These two kinds of functionalities appeared alternately as the terminal groups, with the signals at $\delta = 5.1$ ppm assignable for vinylic and $\delta = 2.7$ ppm for oxirane. Note that the G5-_{ISI} spectrum does not show signals at $\delta = 5.1$ ppm because the grafted chain is homo PSLi (instead of PI-*b*-PSLi) for the final generation to avoid gel formation during storage of the product. A similar phenomenon is also observed for the synthesis from a star-like core. However, it should be pointed out that, while at lower generations the disappearance of the double bond and oxirane signals indicates a high efficiency of grafting reactions, at higher generations the grafting reaction is incomplete due to steric hindrance (*vide infra*). The residual moieties may be shielded by the crowded polymer segment during NMR measurement. Thus, the absence of these signals does not imply a high reaction efficiency.

THF is used as the solvent for the grafting reactions. This is not only because THF promotes the reactivity of the PI-*b*-PS anion towards epoxy groups, but also because THF is a good solvent for the grafted products. Although carbanion reacts with THF very easily (side reaction), it reacts with epoxy groups at a much higher efficiency.¹⁵ Using SEC monitoring, we observe that the grafting reaction is nearly completed within 15 min. Nonetheless, most grafting reactions in this study are allowed to stand overnight to ensure attachment of as many polymer chains as possible.

Fig. 2 shows the SEC traces of dendrimer-like products of different generations after the excess unreacted grafting chains are removed by acetone wash. In some cases fractionation is necessary to completely remove these residual species, while the main peaks remain unchanged during the purification processes (ESI[†]). An excess amount of PI-*b*-PSLi is used both to

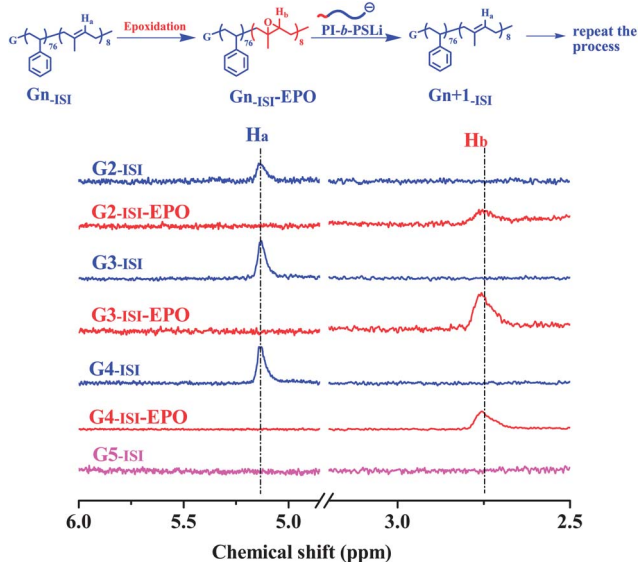


Fig. 1 Monitoring the synthesis of dendrimer-like PS, G_n -_{ISI}, using ¹H NMR spectroscopy in $CDCl_3$.

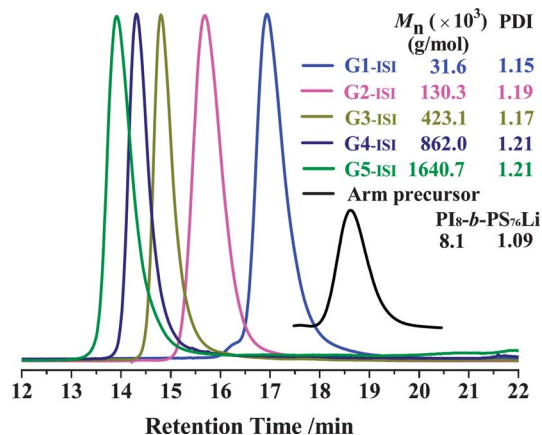


Fig. 2 SEC profiles of dendrimer-like PS of different generations, G_n -_{ISI}, where $n = 1-5$. The samples are purified by removing the excess precursor arm (RT = 18.6 min), as shown in the inset.

ensure the grafting efficiency and to make up for the destruction of the existing hydroxyl groups in the grafting reactions of the previous generations. The molar ratio of PI-*b*-PSLi to epoxide groups is 2 : 1 for G2 and G3, and 3 : 1 for G4 and G5. It is clear that the molecular weight shifts to higher values, while maintaining a narrow distribution along with the generation growth. Because the same stock solution of PI₈-*b*-PS₇₆Li is used as the grafting chain throughout the process, the increase in molecular weight is solely a consequence of the divergent growth of the dendritic structure through “end-grafting” reactions.

It should be noted that the narrow and monomodal distribution in SEC may not reflect the real structural heterogeneity of the dendrimer-like products. SEC separates polymer components according to their hydrodynamic volumes. This mechanism is incapable of resolving structural differences when the two components have similar sizes. It has been demonstrated that temperature gradient interaction chromatography (TGIC) is a more suitable method to analyze the possible defects in branched polymers.^{12d,12e,16} The TGIC results for G3-_{star} are shown in Fig. 3. There are two peaks on the diagram, a main peak and a small side peak, the latter having

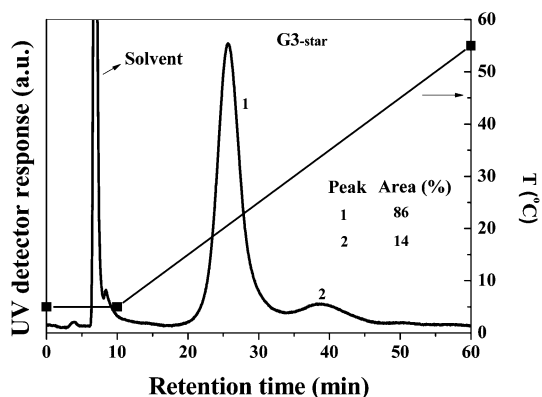


Fig. 3 TGIC diagram of G3-_{star}. The peak areas are integration results after deconvolution using the Gaussian model distribution function.

relatively larger molecular weight. The side peak may be attributed to intermolecular coupling during the polymerization or sample storage. The main peak is asymmetric and shows a “tailing effect” at the larger molecular weight side. The “tailing effect” implies structural heterogeneity caused during the polymerization. In this synthesis, the starting material for the branching reaction is a PI oligomer or PI block. The MALDI-TOF MS results show that the DP of the PI segment varies from 5 to 14 (number average $DP_n = 8$ and $PDI = 1.07$, ESI[†]). The distribution will be inherited during the subsequent epoxidation and grafting reaction. In addition, incomplete reaction caused by steric hindrance and the occasional quenching and coupling events during the polymerization also lead to imperfections in the final product.

Dendrimer-like polystyrenes up to 5th generation are synthesized from both triblock and star-like cores. Theoretical and measured molecular weights are given in Table 1. The molecular weights measured by SEC (PS calibration) are remarkably smaller than those obtained by Zimm plot from light scattering, a feature correlated to the smaller hydrodynamic volume of a dendritic structure than that of the linear polystyrene used in SEC calibration. In contrast, the molecular weights measured by light scattering are closer to the theoretical values from the 1st to 3rd generations, while discrepancies are observed for the 4th to 5th generations. This may indicate that the grafting efficiency decreases along with generation growth due to increasing steric hindrance, which would cause defects in the desired dendritic products. Indeed, the number of arms calculated from the light scattering results is only one-half and one-fifth of the theoretical values for **G5_{ISI}** and **G5_{star}**, respectively. The larger difference in the latter is caused by greater steric hindrance in the products from the star-like core.

Molecular conformation in solution

The shape and internal structure of the dendrimer-like products are studied by static and dynamic light scattering on dilute solutions of the products. The results are presented in Fig. 4 and

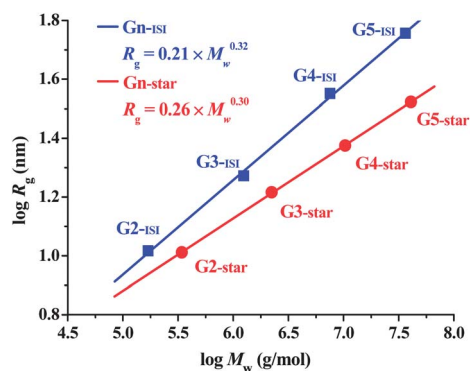


Fig. 4 Dependence of radius of gyration on molecular weight on a log–log scale.

5 and Table 2. The dependence of radii of gyration, R_g , on molecular weight is plotted in Fig. 4 on double logarithmic scale for both series from different cores. Good linearity is observed with slopes of 0.32 and 0.30 for **G_{n,ISI}** and **G_{n,star}**, respectively. As the spacer chain lengths are constant (e.g., 8500 g mol⁻¹ for the former and 5700 g mol⁻¹ for the latter), the dependence on molecular weight is rescaled to the dependence on the number of arms for different generations. These power laws are very close to the simulation,¹⁷ SANS¹⁸ and SAXS¹⁹ experimental results for the isolated dendrimers, which gives a scaling law of $R_g \sim N^{1/3}$, where N is the total number of monomers. This corresponds to a fractal number of 3, indicating that the conformation of the dendrimer-like products adopts a three-dimensional globular state for the 2nd to 5th generations.

The combination of SLS and DLS is used to probe the internal structure of the dendrimer-like products in THF solution. The R_g/R_h ratio generally reflects the conformation of the macromolecules in dilute solution. The ratio equals 1.78–2.05 for a random coil of linear chain in good solvent, whereas the ratio is 0.778 for a homogeneous hard sphere, and 0.977 for dendrimers of high generation (Gaussian “soft sphere”).²⁰ The results of R_g/R_h are listed in Table 2 and are shown in Fig. 5. It is clear that, for the samples made from the star-like core, the

Table 1 Dendrimer-like polymers prepared by “end-grafting” methodology using ISI-type and star-like core

Entry	$M_{\text{theo.}}$ ($\times 10^3$ g mol ⁻¹)	$M_{n,\text{SEC}}^d$ ($\times 10^3$ g mol ⁻¹)	PDI_{SEC}	$M_{w,\text{MALLS}}^e$ ($\times 10^3$ g mol ⁻¹)	$N_{\text{arm,theo.}}^f$	$N_{\text{arm,obs.}}^g$	dn/dc (mL g ⁻¹)
G1_{ISI} ^a	30	32	1.15	29	2	—	0.170
G2_{ISI}	166	130	1.19	169	18	20	0.180
G3_{ISI}	1254	423	1.17	1242	146	146	0.184
G4_{ISI}	9958	862	1.21	7512	1170	884	0.184
G5_{ISI} ^b	79 590	1641	1.21	36 270	9362	4267	0.175
G1_{star} ^c	49	34	1.19	50	8	9	0.154
G2_{star}	414	132	1.20	343	72	60	0.181
G3_{star}	3332	314	1.16	2230	480	391	0.181
G4_{star}	26 679	592	1.21	10 340	3128	1814	0.175
G5_{star}	213 628	992	1.29	40 770	35 896	7153	0.178

^a **G_{n,ISI}** are dendritic products of n -th generation with the ISI-type core and PI₈-*b*-PS₇₆Li as the arm ($M_{n,\text{arm,NMR}} = 8.5 \times 10^3$ g mol⁻¹). ^b The incoming arm is PS₈₃Li ($M_{n,\text{arm,SEC}} = 8.7 \times 10^3$ g mol⁻¹). ^c **G_{n,star}** are dendritic products of n -th generation with the star-like core and PI₈-*b*-PS₁₀₉Li ($M_{n,\text{arm,NMR}} = 5.7 \times 10^3$ g mol⁻¹) as the arm. ^d $M_{n,\text{SEC}}$ was measured on a Waters SEC system calibrated by linear PS standard. ^e $M_{w,\text{MALLS}}$ was determined on a DAWN HELEOS (14–154°) (Wyatt multiangle laser light scattering detector, He-Ne 658.0 nm). ^f Theoretical total number of arms is calculated by $N_{\text{Gn-isi,arm,theo.}} = 2\sum 8^{(n-1)}$ and $N_{\text{Gn-star,arm,theo.}} = \sum 8^n$. ^g Observed total number of arms is obtained as $N_{\text{arm,obs.}} = M_{w,\text{Gn}}$ (by MALLS)/ $M_{n,\text{arm}}$.

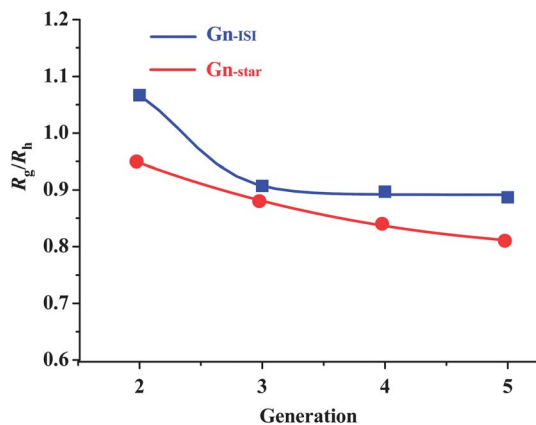


Fig. 5 Dependence of R_g/R_h ratios on generation (lines for guidance, the data refer to Table 2).

R_g/R_h ratio decreases from 0.95 to 0.81 when the generation increases from 2 to 5. Thus, the conformation of lower generations, e.g., **G2-star**, is very close to the “soft sphere” usually observed for a regular dendrimer of high generation. This may be attributed to the larger branching functionality ($1 \rightarrow 8$) both at the core and the branch points, causing intensive branching density in the product. The chain density increases further along with the generation growth, and reaches a more compact conformation which is close to a “hard sphere” at the 5th generation. In addition, the R_g/R_h values of the samples using star-like cores are always lower than those using triblock cores, demonstrating a more compact conformation in the former due to higher functionality of the star-like core and shorter length of the arms (M_n of PI-*b*-PSLi is 5700 and 8500 g mol⁻¹ in the former and latter systems, respectively). Indeed, the chain densities within each single molecule, ρ , calculated on the basis of globular conformation (refer to Table 2 notes), are remarkably larger for the products with star-like cores than those with linear triblock cores, as shown in Table 2.

Molecular dynamics simulation is employed to investigate the conformation of dendrimer-like polymers (**G3-star**, **G4-star** and **G5-star**). Assuming the volume exclusion effect plays a

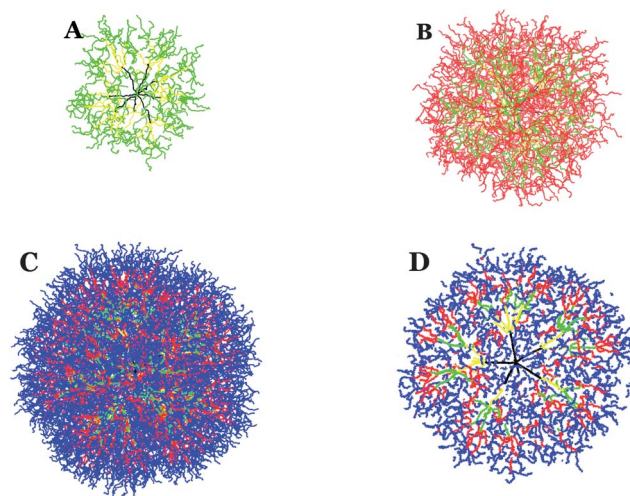


Fig. 6 Simulation snapshots of dendrimer-like products by molecular dynamics method. (A) **G3-star**. (B) **G4-star**. (C) **G5-star**. (D) Cross-section of **G5-star** at the core.

dominant role in the final conformation, we consider only bond and pair potential in the simulation. Chemical heterogeneity caused by the PI segment and the resulting hydroxyl groups are ignored. The atomic numbers of **G3-star**, **G4-star** and **G5-star** are 3969, 16769 and 67969, respectively. Their ratios are close to practical arm numbers measured by light scattering (Table 1). Fig. 6 shows the simulation snapshots of different generations. It is clear that the outermost surface is occupied mainly by the highest generation, but the segments of the highest generation can be found throughout the whole molecule *via* chain back-folding, as illustrated in the simulated cross-section of **G5-star** (Fig. 6D). It is also interesting to note that the chain segments belonging to the first generation take a more extended conformation. This is because the high local chain density at the core induces stronger monomer unit repulsion that prohibits conformational elasticity.²² In regular star-like polymers, the radial decay in chain density leads to a radial decrease of branch extension.²³ The branches are rigid near the core and flexible at the far ends. In the molecular structure of this study, the

Table 2 Results of light scattering of dendrimer-like products

Name	M_w ($\times 10^3$ g mol ⁻¹)	R_h^a (nm)	R_g^b (nm)	PDI	g^c	R_g/R_h	ρ_h^d (g cm ⁻³)	ρ_g^e (g cm ⁻³)
G1-1SI	29.4	4.3	—	0.07	—	—	0.147	—
G2-1SI	169	9.7	10.4	0.06	0.34	1.07	0.074	0.060
G3-1SI	1242	20.6	18.7	0.03	0.12	0.91	0.057	0.076
G4-1SI	7512	40.0	35.6	0.04	0.06	0.90	0.047	0.066
G5-1SI	36 270	64.4	57.1	0.02	0.03	0.89	0.054	0.078
G1-star	50.1	6.0	—	0.10	—	—	0.092	—
G2-star	343	11.9	11.3	0.03	0.18	0.95	0.081	0.095
G3-star	2230	22.6	19.9	0.04	0.07	0.88	0.077	0.113
G4-star	10 340	36.8	30.9	0.04	0.03	0.84	0.083	0.140
G5-star	40 770	57.3	46.5	0.03	0.01	0.81	0.086	0.162

^a Determined by DLS at a scattering angle of 90° at 30 °C in THF. ^b Determined by Zimm plot at 30 °C in THF. ^c $g = R_g^2 \text{dendrimer-like} / R_g^2 \text{linear}$, where $R_{g, \text{linear}} = 2.09 \times 10^{-2} \times M_w^{0.56, 21}$. ^d Chain density within each single dendrimer-like molecule is calculated as $\rho_h = M_w / (N_A (4/3) \pi R_h^3)$, where M_w is the weight-average molecular weight measured by MALLS and N_A is Avogadro's number. ^e Chain density within each single dendrimer-like molecule is calculated as $\rho_g = M_w / (N_A (4/3) \pi R_g^3)$.

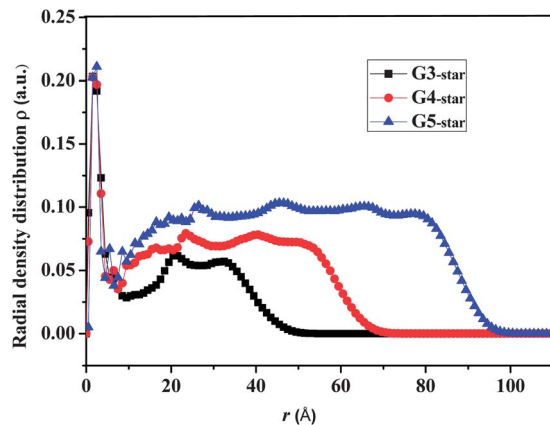


Fig. 7 Simulated radial density profiles of the dendrimer-like PS by the molecular dynamics method.

branches interconnecting different generations are “fixed” by the branch points at both ends, leading to higher extension of the branches. In addition, each branch point behaves like a core and gives higher local chain density and thus, extended chain conformation. The chains of the highest generation are most flexible because of one free end.

Fig. 7 presents the radial density distribution profiles of **G3_{star}**, **G4_{star}** and **G5_{star}** after an equilibration period of 9 μ s. There are three notable characteristics in the profiles. First, the highest chain density is found near the core, as expected for chain knotting at the core. Second, the main part of a dendrimer-like molecule possesses a nearly homogeneous chain density, in spite of local maxima, which are attributable to the branch points. This homogeneity is a consequence of dynamic equilibrium through back-folding of the chain segments belonging to higher generations. It is obvious that the chain density increases along with generation growth. Third, the chain density decreases monotonically to zero in the outermost region, the size of which seems independent of the generation number. Thus, the simulation results are very much in agreement with the results reported by Murat and Grest, demonstrating a filled sphere, instead of a hollow core, for the dendrimers.^{17a}

A unique property of dendrimers and dendrimer-like polymers is that their intrinsic viscosities do not monotonically depend on molecular weight.^{1b,2b,3a,3b,7d,24} The Mark–Houwink–

Sakurada equation is not applicable for dendritic products. Fig. 8 shows the variation of intrinsic viscosity, $[\eta]$, measured by an on-line differential viscometry detector coupled with SEC, along with the generation. For both series of dendrimer-like polymers (e.g., with a star-like core or linear triblock core), the viscosities pass through maxima at **G3** and **G4** and then decrease at **G5**. This behavior correlates well with a highly crowded chain conformation at higher generations. According to Mourey and co-workers, the intrinsic viscosity of a dilute solution of dendrimers is written in a similar way to Einstein's equation for hard spheres,^{24b}

$$[\eta] = \frac{2.5N_a V_h}{M_w}, \quad (1)$$

where V_h is hydrodynamic volume, M_w is the molecular weight and N_a is Avogadro's constant. The parabolic variation of intrinsic viscosity with molecular weight is a consequence of increasing V_h proportionally *versus* increasing M_w exponentially along with generation growth. However, dendrimers are far from ideal hard spheres, and the expression of V_h as a function of molecular weight has never been derived. Theoretical studies by An and co-workers propose two component contributions to the hydrodynamic volume of a solvent-draining dendrimer, *i.e.*, the actual total volume of monomers (Debye contribution) and the volume of solvent molecules dragged by the dendrimer (Einstein contribution).²⁵ In general, a dendrimer molecule consists of a non-draining core and a free-draining shell, and moves with the solvent molecules in the core as a whole.²⁶ The maximum intrinsic viscosity reflects the competition between the increase of the overall hydrodynamic volume and the increase of segmental density with the generation propagation, although defects exist at higher generations.

The branching effect is usually described as contraction factor, g or g' , defined as the ratio of squares of gyration radii, or intrinsic viscosities of dendrimer-like polymers to that of the linear counterparts, respectively. As shown in Table 2 and Fig. 9, both g and g' values decrease with generation growth. At 5th generation these values are extremely low. In addition, marginal decreases in both g and g' are observed for the products from the star-like core, accounting for the more compact conformation due to the higher functionality of core.

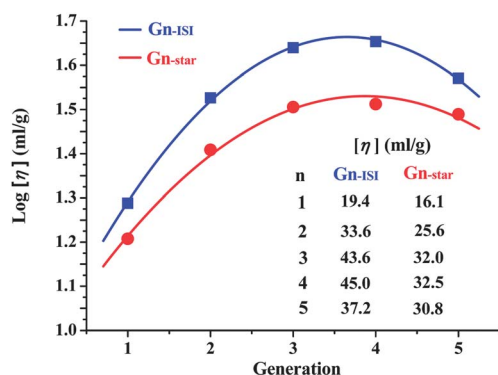


Fig. 8 Dependence of viscosities on generation numbers on a semi-log scale (lines for guidance).

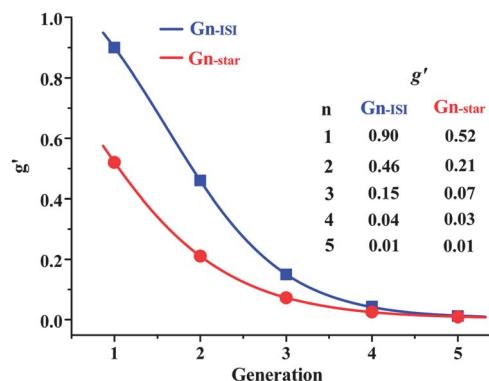


Fig. 9 Decreases in contraction factors g' as functions of generation numbers (lines for guidance).

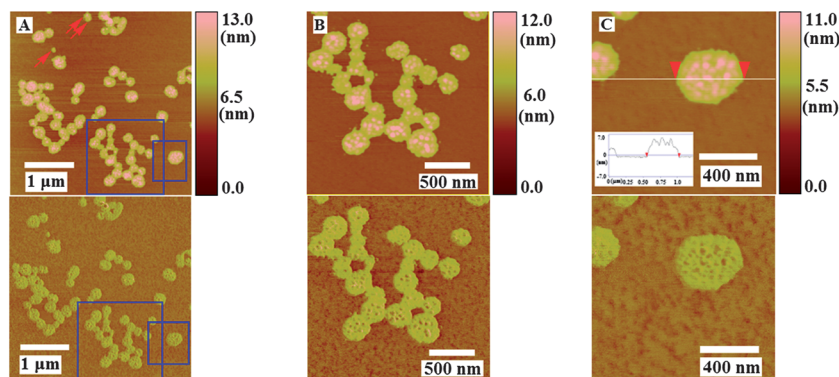


Fig. 10 AFM images of dendrimer-like polymer **G4-star** on mica (AFM is performed in tapping mode), B and C are enlargements of the parts in the frames.

AFM observation of dendrimer-like polymers

AFM is performed on dendrimer-like products spin-coated on a mica surface from dilute chloroform solution (0.1 mg mL^{-1}). As shown in Fig. 10, round-shaped objects are observed with varying diameters from 100 to 400 nm. The heights of the objects are *ca.* 4 nm, illustrating that dendrimer-like products adopt a flattened conformation on the surface due to collapse of the polymer segments in the vertical direction. This phenomenon is consistent with many previous reports on regular dendrimers and dendrimer-like polymers.^{2d,7d,7e,27} Nonetheless, the product height is notably higher than those reported for dendrimer-like polymers in our previous study¹⁴ and those observed by Hirao and co-workers^{7d,7e} (normally *ca.* 1 nm). This is a consequence of higher chain density, associated with larger branch functionality in the present study.

The round-shaped objects can be classified into two series in terms of their diameters. Those with diameters of around 100 nm (labeled by arrows) may be single molecules because their sizes are smaller than the theoretical values of fully extended conformation (*ca.* 120 nm). These smaller sizes are still larger than the hydrodynamic radius (*ca.* 40 nm in Table 2) due to lateral extension of the chain segment on the surface. In contrast, the objects with larger diameters (*e.g.*, 200 to 400 nm) may be ascribed to laterally assembled molecules with varying aggregation numbers. These aggregates contain island-like domains of *ca.* 6 nm in height and ~ 30 nm in diameter, scattered on a plateau of *ca.* 4 nm in height (Fig. 10C). The “islands” are formed by the central part of the dendrimer-like molecules through a balance of cohesive energy and conformation entropy during the evaporation of the solvent, whereas the plateaus are formed by the interpenetration of the peripheral parts of the dendrimer-like molecules. Thus, it seems that the dendrimer-like products show a very strong tendency to form aggregates due to the multiplicity of the peripheral segments, although a highly diluted solution is used in spin coating.

Conclusion

This study develops a simple “end-grafting” approach to synthesize dendrimer-like polymers with high branching functionality ($1 \rightarrow 8$ in this case) in a divergent way. This intensive

branching approach facilitates the synthesis of meso-sized dendritic polymers with high chain densities. Imperfection is caused by polydispersity in the PI segment, the precursor for the grafting reaction, and steric hindrance in higher generations. Light scattering and viscometry results concurrently support the conclusion that the dendrimer-like products adopt a compact conformation in solution. Molecular dynamics simulations indicate a homogenous density distribution in the inner structure and decreasing density in the periphery region. Using AFM, we observe single molecules as flattened sphere-like objects. These molecules tend to aggregate laterally to form larger sized objects on a mica surface, with scattered island-like domains formed by the central part of the molecule, surrounded by a plateau formed by the interpenetration of the periphery part.

It is expected that the present method can be extended to the synthesis of dendrimer-like polymers and copolymers with different chemical structures. This versatility arises from the suitable initiation reactivity of polyisoprenyllithium, modified with DPE if necessary, towards a number of monomers such as styrene, dienes, methacrylates, 2-vinylpyridine and ethylene oxide. Therefore, the arms can be various kinds of block copolymer containing a short segment of polyisoprene at the original end. Dendrimer-like copolymers with layered structures, *e.g.*, different chemical compositions for different generations, can be synthesized with different arm combinations without vigorous pre-requisites for the choice of layer sequence. These syntheses are currently under investigation in our laboratory.

Experimental section

Materials

Styrene (National Pharmaceutical, $\geq 99\%$) and isoprene (TCI, $\geq 99\%$) were distilled over CaH_2 and stored at -10°C . Styrene and isoprene were distilled over di-*n*-butylmagnesium ($\text{Mg}(n\text{-Bu})_2$) (Aldrich, 1.0 M in heptane) on the vacuum line before use. Cyclohexane and tetrahydrofuran (THF) were refluxed over sodium with benzophenone as indicator, and distilled from 1,1-diphenylhexyllithium (DPELi, adduct of *s*-BuLi with DPE) on the vacuum line before use. *n*-Butyllithium (*n*-BuLi) (Aldrich, 2.5 M solution in cyclohexane–heptane) was used as received.

sec-Butyllithium (*s*-BuLi) (Aldrich, 1.3 M solution in cyclohexane) was titrated before use. Formic acid (National Pharmaceutical, >88%) and hydrogen peroxide (30%) were used as received.

Measurements

¹H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using CDCl₃ as the solvent and tetramethylsilane as the interior reference.

Size exclusion chromatography (SEC) analysis was performed through three Waters Styragel columns (pore size 10², 10³ and 10⁴ Å), calibrated by narrow polystyrene standards, and equipped with three detectors, including a DAWN HELEOS (14–154°) (Wyatt multiangle laser light scattering detector, He–Ne 658.0 nm), ViscoStar (Wyatt), and Optilab rEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL min⁻¹ at 35 °C. *R_g* was obtained by a Zimm plot given by DAWN HELEOS in the off-line mode. *dn/dc* was determined in Optilab rEX in the off-line mode.

AFM images were obtained with a NanoScope IV (Digital Instruments, Santa Barbara, CA) instrument operated in tapping mode, using the silicon tips of a Model TESP (Digital Instruments) with a tip curvature radius less than 10 nm. A polymer solution (0.01–0.05 mg mL⁻¹ in chloroform) was spin-coated (1500 rpm for 5.0 s and then 2800 rpm for 1.0 min) on a freshly cleaved mica surface.

The MALDI-TOF mass spectrum was obtained from a Voyager DE-STR matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. A 10 μL sample solution (10 mg mL⁻¹ in THF) was mixed with 10 μL dithranol as the matrix (20 mg mL⁻¹ in THF) and 2.0 μL silver trifluoroacetate (10 mg mL⁻¹ in THF). Then 0.50 μL of the mixed solution was dropped onto the plate and dried at ambient temperature. Mass spectra were given by a reflector mode using an acceleration voltage of 20 kV with an appropriate laser power and 1000 pulses were averaged in general.

Dynamic light scattering (DLS) experiments were performed on an ALV-5000 laser light scattering spectrometer equipped with a multi-τ digital time correlation (ALV5000) and a He–Ne laser (λ₀ = 632.8 nm) light source at 30 °C and at a fixed scattering angle of 90°. Before measurement, every sample solution was filtered through 0.2 μm Millipore filters (Millipore Millex-FG, Phobic PTFE) to remove dust. The hydrodynamic radius (*R_h*) and polydispersity index (PDI) were obtained by the CONTIN program. *R_g*s of the samples were also determined on the ALV-5000. The sample solutions were carefully filtered through 0.2 μm Millipore filters (Millipore Millex-FG, Phobic PTFE) until no dust was found by DLS at 30°. After correction by toluene and pure THF from 30° to 150° with a step of 5°, the static light scattering determination was performed in the same conditions to give *R_g*.

For the TGIC analysis,²⁸ a C18 bonded silica column (Nucleosil C18, 7 μm, 1000 Å pore, 250 × 4.6 mm i.d.) was used. The mobile phase was a mixture of CH₂Cl₂/CH₃CN (68/32, v/v, Samchun, HPLC grade) at a flow rate of 0.5 mL min⁻¹. The temperature of the column was controlled by circulating fluid from a programmable bath/circulator (Julabo, F25-HL) through a homemade column jacket. The sample solutions (~2 mg mL⁻¹) were prepared by dissolving the polymers in a small

volume of eluent and the injection volume was 100 μL. The chromatograms were recorded with a LS detector (Wyatt, Treos) and a UV detector (Younglin, UV730D) operating at a wavelength of 260 nm.

Synthesis of PI-*b*-PS-*b*-PI triblock core, star-like core and PI-*b*-PSLi living arm

Glass apparatuses were connected to the vacuum/argon line. All polymerizations were carried out in a flask with a magnetic stirrer bar inside. The flask was dried by four cycles of flaming/Ar-purging/evacuating and rinsed sequentially with a dilute cyclohexane solution of *n*-BuLi and pure cyclohexane.

Isoprene (0.50 mL, 0.34 g) was polymerized with the initiation of *s*-BuLi (0.5 mL, 1.30 mmol mL⁻¹ cyclohexane solution) in cyclohexane (60 mL) at 35 °C for 1 h, yielding polyisoprene (PI₈Li) with *M_n* = 610 g mol⁻¹ and PDI = 1.07 (by MALDI-TOF MS).

Anionic polymerization of styrene (22.0 mL, 19.5 g, 0.19 mol) (distilled over 2 mL 1.0 M heptane solution of dibutyl magnesium) initiated by PI₈Li (3.88 mmol) at 40 °C for 4 h yielded PI-*b*-PSLi. Two kinds of PI-*b*-PSLi were prepared by changing the feed amounts of styrene. PI₈-*b*-PS₄₉Li: *M_{n,NMR}* = 5.7 × 10³ and PDI = 1.09; PI₈-*b*-PS₇₆Li: 8.5 × 10³ g mol⁻¹, PDI = 1.10. PI-*b*-PSLi was used as living arms in the subsequent grafting reaction.

PI₈-*b*-PS₂₇₁Li (0.65 mmol) was mixed with isoprene (0.5 mL) (distilled over 2 mL 1.0 M heptane solution of dibutyl magnesium) in a flask and the reaction mixture was heated at 35 °C for 1 h before being deactivated by degassed methanol. After precipitation into methanol, the product, PI-*b*-PS-*b*-PI, was obtained and dried under vacuum. *M_{n,SEC}* = 31.6 × 10³ g mol⁻¹, PDI = 1.15. This polymer was used as a triblock core in the synthesis of dendrimer-like polymers.

PI₈Li (1.3 mmol) in 30 mL cyclohexane was terminated with degassed methanol, and dried by evaporation and in a vacuum oven. The collected PI₈ (0.4 g) was dissolved in toluene (30 mL) and mixed with HCOOH (2 mL) and H₂O₂ (4 mL) at 25 °C for 0.5 h then 35 °C for 0.5 h. The reaction mixture was washed by deionized water (20 mL × 3) and the organic layer was collected. The epoxidation product (PI-EPO) was obtained (0.30 g, yield: 61%) after removal of toluene and dried under vacuum at a temperature below 35 °C. PI-EPO (0.05 g, epoxy group 0.60 mmol) was dissolved in THF (40 mL) and mixed with PI-*b*-PSLi living arm (1.2 mmol, 95 mL cyclohexane solution). The reaction stood overnight at 35 °C and then deactivated using degassed methanol. The product was obtained by precipitation from acetone and washed with acetone three times (in some cases fractionation is needed using a varying amount of methanol-toluene) (3.3 g, yield: 89%) (*M_{n,SEC}* = 3.4 × 10⁴ g mol⁻¹, *M_{w,MALLS}* = 5.0 × 10⁴ g mol⁻¹, PDI = 1.19). The SEC results of the star-like core synthesis are given in the ESI†. The product was used as a star-like core in the synthesis of dendrimer-like polymers.

Epoxidation process

Epoxidation of the PI segment was accomplished using H₂O₂-HCOOH in toluene. Using the epoxidation of G1-*ISI* (*M_{n,SEC}* = 31.6 × 10³ g mol⁻¹, PDI = 1.15) (Table 1, Entry 1) as an example,

G1_{-ISI} (1.0 g) was dissolved in 30 mL of toluene. Excess amounts of HCOOH (1 mL) and H₂O₂ (1 mL) were added at 25 °C for 0.5 h, and the temperature was raised to 35 °C for 0.5 h. The reaction mixture was washed by deionized water (20 mL × 3) and the organic layer was collected. The epoxidation product (**G1_{-ISI}-EPO**) was obtained after precipitation in methanol and dried under vacuum at a temperature below 35 °C. $M_{n,SEC} = 32.1 \times 10^3 \text{ g mol}^{-1}$, PDI = 1.14.

Divergent “end-grafting” reaction

The grafting reaction was carried out in THF. Using the **G2** synthesis as an example, dry **G1_{-ISI}-EPO** (0.4 g) was dissolved in THF (80 mL) and excess pre-synthesized PI-*b*-PSLi living arm was added (molar ratio of Li to epoxide is ~2 : 1). The reaction stood overnight at 35 °C and was then deactivated using degassed methanol. The product was obtained by precipitation from acetone and was washed with acetone two or three times and dried overnight at room temperature. $M_{n,SEC} = 130.3 \times 10^3 \text{ g mol}^{-1}$, PDI = 1.19.

Repeating the “end-grafting” and epoxidation processes afforded dendrimer-like polymers with growing generations. The molar ratio of living chains to epoxide groups was 2 : 1 for **G2** and **G3**, and 3 : 1 for **G4** and **G5**. In some cases fractionation using methanol-toluene (the volume ratio may vary from case to case) was necessary to remove unreacted arms.

Molecular dynamics simulation

A molecular dynamics simulation on the conformation of the dendrimer-like polymers (**G3_{-star}**, **G4_{-star}** and **G5_{-star}**) was performed using the program LAMMPS. Only bond potential and pair potential were considered, and the constitutional units were coarse-grained into the uniform particles, whose parameters were derived from the parameters of carbon atoms in OPLS.²⁹ The particle numbers of **G3_{-star}**, **G4_{-star}** and **G5_{-star}** are 3969, 16 769, and 67 969, respectively. The simulation was performed in the NVT ensemble (*i.e.*, the temperature was 300 K), and the time-step was 1 ps. The initial condition for each generation was based on the equilibrium conformation of the previous generation. The relaxation was accomplished separately for the inner and outer generations for the initial period of 1 μs. Then, the system experienced an entire relaxation normally longer than 9 μs.

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